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(54) Title: MANUFACTURE OF COMPOSITE BOARDS

(57) Abstract

Annual plant material such as straw is treated to improve bondability with composite forming bonding resins by subjecting to a liquid medium containing sufficient of a sufficiently strong acid, alkali or surfactant to remove substantially waxy or silica layers.

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Manufacture of Composite Boards

The present invention relates to a method of manufacturing composite boards including improving the bondability of annual plant fibrous material such as straw.

Many treatments have been described in the literature to improve the bondability of lignocellulosic materials in both particle and fibre form with synthetic resins. (SIMON AND L. PAZNER): (Activated self-bonding of wood and agricultural residues - Holzforschung 48:82 - 90, 1994) investigated the influence of the hemicellulose content of the self-bonding behaviour of different raw materials including annual plants and concluded that there is a straight forward relation between the hemicellulose content in the raw materials and the bonding strength of composites prepared therefrom. According to this work hemicelluloses do have adhesive properties, however, bonds created using hemicellulose adhesives have almost no wet strength.

In a recent publication LIAN ZHENGTIAN and HAO BINGYE: (Technology of rice-straw particleboards bonded by Urea-formaldehyde resin modified by isocyanate - Paper presented at the Symposium Pacific Rim Bio-Based Composites, Rotorua, New Zealand 9 - 13 November 1992 Symposium Proceedings, page 295 - 301, 1992) mentioned that slight improvement of bondability of straw can be achieved by destroying the waxy layers encirculing the stem of straw, however, the bondability was still very poor and the boards made still could not meet the requirements of common standards.

Treatments with alkaline or acidic agents of lignocellulosic materials before formation of composite materials have been proposed as in WO 93/25358, WO

91/12367 or DE 4211888 but this has been discussed in relation to the structure of wood structure materials. The effect of acid or alkaline on the structure of materials such as straw with its waxy/silica layers has not been considered.

In Applicant's application number GB 9607566.8 it was disclosed that thermal treatment of straw or other annual plant fibres with water or steam at temperatures between 40 - 120°C, preferably between 60 - 120°C, with simultaneous or subsequent defibration of the straw using high shear forces opens up the morphological structure of straw and increases the affinity towards bonding.

Cellulosic materials such as straw have been treated with mildly acidic or alkaline materials before use for various purposes. In U.K. Patent GB 709569A straw is treated with hypochlorous acid and soda solution in bleaching for paper manufacture. There is no reference to resin-bonded board manufacture. In U.K. Patent GB 2084212A there is disclosure of manufacture of low density panels from rice hulls with a two-component binder using lime chloride to effect some de-waxing but emphasising that the process must avoid the removal of silica. There is no disclosure of manufacturing medium or high density boards bonded with amino-resins.

Defibration means disruption of the morphological structure of annual plant fibres, straw leading to the creation of individual fibres. In the original morphological structure of, for example, straw, the waxy and the silica layer encircling the straw inhibit sufficient direct contact between the binder and the straw fibres. In the earlier application it was disclosed that thermal treatment combined with high shear forces disrupts the original morphological structure of straw leading to higher accessibility of individual

fibres to the binder and consequently, an increase in the affinity of straw towards bonding. The process of opening up the morphological structure of straw is similar to that of pulping wood for paper making.

In a preferred embodiment of the invention of the earlier application it is disclosed that the properties of the boards made from straw could be further improved if the straw was treated or pre-treated with a dilute solution of sodium hydroxide containing 0.01 - 2% NaOH based on the straw material.

It was further disclosed that other alkaline materials other than sodium hydroxide could be also used to achieve the same effect. It was disclosed that such chemicals could be formaldehyde catchers such as urea and other catchers well known in the art.

A problem with the processes of the earlier application is that high and therefore costly energy input into the process is required in order to provide the required high shear forces. As the skilled operative would be aware these types of forces can be applied, for example, by twin screw extruders, disc refiners or other suitable attrition mill devices like Ultra Turrax.

The present invention provides a process for the manufacture of composite boards in which annual plant and/or agri-waste material is treated to improve bondability to synthetic or natural binders by subjecting the material to treatment with an aqueous medium containing an agent capable of removing waxy or silica layers from the material, which agent is a strong acid, a strong alkali or a surfactant or a combination of acid or alkali and surfactant and the treatment is continued until the waxy or silica layers are sufficiently removed so as not to interfere with the bond to the binder.

The preferred agent is a combination of strong acid or alkali and surfactant.

The process of the invention can be applied either to undefibrated plant material that is plant material in which the stalks are merely chopped or to defibrated plant material in which the original material has been broken down to individual fibres.

Modification of the process of the present invention is the addition of such an agent to a material while it is being subjected to high shear treatment providing such agent is a combination of a surfactant with an acid or alkali to reduce the energy consumption or improve properties of the boards.

According to another aspect of the invention therefore there is provided a process for the treatment of annual plant material to improve bondability to synthetic or natural binders comprising subjecting the material to treatment with a surfactant in a liquid acidic or alkaline dispersion or solution before or during at least part of an attrition treatment of the material to reduce the energy consumption or improve properties of the boards.

In a particular embodiment of the invention there is provided a process in which the plant material is treated with an aqueous system containing acid or non-alkaline surfactant. In this process the treatment can precede or be simultaneous with a high shear treatment of the material to effect defibration to reduce the energy consumption or improve properties of the boards.

In one embodiment of the invention there is provided a combination of strong alkali (e.g. NaOH) and a

surfactant to treat the plant material.

In another embodiment there is provided the use of a strong acid in high strength (for example 36% by weight solution in water of hydrochloric acid). By high strength is meant a solution in water of the highest strength possible with risk of damage to the straw (for example at too great a concentration sulphuric and nitric acids for example could damage the basic straw structure).

Those skilled in the art will have no difficulty in selecting an appropriate strength of acid to achieve de-waxing/de-silification without fibre damage.

In another aspect of the invention there is used a combination of strong acid and surfactant.

In another aspect of the invention there is employed a surfactant which is sufficiently strong to remove waxy layers in straw material.

The effectiveness of the de-waxing or de-silification agent can be verified by achieving a water absorption (% weight gain on soaking in water) of at least 200% or by forming a board and verifying that the board has a certain IB (Internal Bond) strength. The IB strength is the tensile strength perpendicular to the plane of the board, e.g. according to EN312-2 for 19mm-thick particleboard at least an IB strength of 0.24N/mm^2 is considered to be necessary.

Acids which can be employed include strong inorganic acids such as sulphuric acid or hydrochloric acid and strong organic acids such as formic, acetic or sulfonic acid. Surfactants which can be employed in the invention are those surface active agents which are sufficiently

powerful to effect the removal of wax or silica layers from the surface of straw. In particular some surfactants are not easily dispersible or soluble in water or other solvents and should be added to water or solvent along with an alkaline or acidic agent to enable adequate dispersion or solution. A typical surfactant is o,p-dodecyl sulfonic acid but this is only exemplary of the well known agents. This surfactant when used with sodium hydroxide, as alkali was very effective. Other surfactants are alkyl benzene sulphonic acid for example with sodium hydroxide; cetyl trimethyl ammonium chloride for example with hydrochloric acid. This surfactant can be employed by itself for example a fatty alcohol surfactant can be selected from cationic, anionic or neutral surfactants which one skilled in the art would appreciate, given the teaching of the invention would be likely to affect the waxy/silicious agents. Alkalis which can be employed include sodium hydroxide or other strong inorganic alkalis, ammonia or organic strongly alkaline materials.

The active agents can be contacted with the straw in either a pre-treatment step or as a part of a defibration treatment step. If the fibrous material is to be brought into contact with active agent as a pre-treatment step then it is convenient to use a tank. A tank can be filled with the appropriate chemical and then the residence time of the fibrous material in the tank can be adjusted accordingly depending on the actual chemical used, the concentration of the chemical and the temperature of the acidic or alkaline solution or the temperature of the aqueous wetting agent solution. It will be recalled that the purpose of the treatment is to dissolve or otherwise remove the waxy layer and/or the silica layer from the surface of the plant fibres.

An important aspect of the invention is that in case

of acid curing binders the plant material after treatment is adjusted (if necessary) to a pH of 3-8. This can be achieved by addition of either alkali or acid as appropriate or by extensive washing.

It is also important that the plant material particularly straw is chopped or cut to a length of less than 10cm preferably between 0.5cm and 5cm. It is also possible to split the straw stalks in the middle (lengthwise) to make the interior of the fibre accessible to subsequent treatment.

Material that is used in the process of the invention is annual plant material and/or agri-waste such as rice, straw, rice husks, wheat straw, rice straw, barley straw, corn residues, miscanthus, sorghum, sunflower etc. However, most preferably, straws are utilized in the processes of the invention.

High shear devices which can be used when required include high shear attrition systems discussed in the earlier application UK 9607566.8. However, it is also possible to use attrition mills which employ less energy than high shear systems. Such attrition mills are well known in the art.

As mentioned if an attrition method is to be used in the process of the invention then the fibres pre-treated by acid or alkali and/or wetting agent can be subjected to processing through the attrition mill or alternatively the acid/alkali/wetting agent treatment chemicals can be contacted with the fibres as they enter the attrition mill.

After the acid or alkaline wetting agent treatment and/or defibration, optionally by attrition the fibres can be dried using conventional dryers used in

particleboard factories, e.g. drum dryer, or a tube dryer like that used in medium density fibreboard mills. From then onwards, the dried fibres follow the conventional procedure as for the production of particleboard, medium or high density fibreboard.

Materials particularly straw treated in accordance with this invention have improved bondability to synthetic and natural bonding agents and isocyanate binders.

Binders which can be used to bond treated straw are formaldehyde-based resins such as urea-formaldehyde resins (UF-resins), melamine-urea-formaldehyde resins (MUF-resins), melamine-formaldehyde resins (MF-resins), phenol-formaldehyde resins (PF-resins), melamine-urea-phenol-formaldehyde resins (MUPF-resins), tannin-formaldehyde resins (TF-resins) and isocyanate binders. The binders can be added in the amount of 5 - 25% based on dry straw material. The invention is particularly applicable to amino resins.

The straw can be mixed with the binder when the straw is in the high shear machine when that is employed or in a separate blender.

Addition of a sizing agent is not obligatory but can be added if necessary either in the defibration treatment or separately.

Test for Water Absorption

As mentioned earlier a method of assessing the effectiveness of a treating agent is to measure the water absorption of the treated material.

TEST

Samples of treated straw are dried at 65°C for 48hours. This will usually achieve a moisture content of 5% (dry basis).

Small representative samples of approx. 3.0g of material are introduced in a distilled water bath (of 23°C), and soaked for 30 min. The material is then removed from the bath. The excess water is removed with a vacuum system, and the fibre samples were weighed to estimate the degree of water absorption (as % wt. gain). The higher the degree of dewaxing the higher the degree of water absorption.

As already stated the achievement of a minimum IB-strength (see the Example for measurement of this value) of 0.24 N/mm^2 for 19mm particleboard is also a measure of the effectiveness of removal of wax and/or silica.

The invention will now be illustrated by the following Example which, however, is merely illustrative and not limiting of the invention.

EXAMPLE

Wheat straw was chopped in a hammermill to have a homogenous size where no fibre had a size longer than 10 cm, (preferably between 0.5 and 5cm). The material was dried in an oven at 65°C for 48 hrs. The moisture content of the material was around 5%. Batches of 2 kg each of the dried material were mixed with 40 kg of water in a drum and each was then treated with one of the following chemical (combinations) (Table 1).

TABLE 1: Conditions for the chemical treatment

No	Chemical treatment	Details
1.	Lime hydrate, Ca $(OH)_2$	5g/liter or 200g total
2.	Lime chloride, Ca Cl_2	5g/liter or 200g total
3.	Sodium carbonate, Na_2CO_3	5g/liter or 200g total
4.	Sulfonic acid + NaOH	5g/liter or 200g total of each of the two chemicals
5.	Hydrochloric acid pure (36%)	5g/liter or 200g total
6.	Hydrochloric acid with a surfactant (mainly cetyl-trimethyl- ammonium chloride)	5g/liter or 200g total of each of the two chemicals
7.	Non ionic surfactant (mainly a fatty alcohol)	5g/liter or 200g total

Treatments 1, 2 and 3 were for comparison with the teaching of GB 709569A and GB 2084212A

The treatments were carried out for 24 hours. After the treatments the materials were washed with water. Then, to each batch 40kg of water was added and the pH of the mixture was adjusted around 5 with the addition of either alkali or acid. The resulting mixture was strained and dried in an oven. The degree of dewaxing was checked with the method described above. The moisture content level of all samples tested after drying was 5% by weight (on dry basis).

TABLE 2: Water absorption (% wet. gain) of straw treated with different dewaxing agents for determining the degree of dewaxing:

No	Chemical treatment	% Weight gain
1.	Lime hydrate, Ca $(OH)_2$	110
2.	Lime chloride, Ca Cl_2	100
3.	Sodium carbonate, Na_2CO_3	130
4.	Sulfonic acid + NaOH	360
5.	Hydrochloric acid pure (36% by weight) in H_2O	270
6.	Hydrochloric acid with one surfactant (mainly cetyl-trimethyl- ammonium chloride)	340
7.	Non ionic surfactant (mainly a fatty alcohol)	280
8.	Untreated (control)	90

These results proved clearly that the treatments of the invention removed most of the wax while the chemicals mentioned in the two U.K. patents do not remove significant amounts of wax. As dewaxing agent, the combination of sulfonic acid with sodium hydroxide shows the highest dewaxing.

With the straw treated by each of the above treatments lab boards were prepared with a thickness of 16mm as follows:

After the straw has been dried to a moisture content of approximately 4% it was placed in a Loedige blender and a urea formaldehyde resin was applied with a spraying

system. The resin was catalyzed with an ammonium salt to accelerate the curing. The glued material was then formed to boards and the boards were pressed in a hot press. The initial temperature of the press was 200°C.

After the pressing, the boards were left to cool and then representative samples 50 by 50 mm were cut and the strength was tested with a Zwick instrument. The results are summarized in the table below (Table 3)

TABLE 3: RESULTS OF BOARDS PREPARED OF STRAW TREATED WITH THE VARIOUS METHODS

No	Chemical treatment	IB strength N/mm^2
1.	Lime hydrate, $Ca(OH)_2$	0.12
2.	Lime chloride, $CaCl_2$	0.11
3.	Sodium carbonate, Na_2CO_3	0.13
4.	Sulfonic acid + NaOH	0.45
5.	Hydrochloric acid pure (36%)	0.33
6.	Hydrochloric acid with one surfactant (mainly cetyl-trimethyl- ammonium chloride)	0.40
7.	Non ionic surfactant (mainly a fatty alcohol)	0.36
8.	Untreated (control)	0.10

Only those boards prepared using straw treated in accordance with the invention achieved the necessary strength.

WHAT IS CLAIMED:

1. A process for the manufacture of composite boards in which annual plant and/or agri-waste material is treated to improve bondability to synthetic or natural binders by subjecting the material to treatment with an aqueous medium containing an agent capable of removing waxy or silica layers from the material, which agent is a strong acid, a strong alkali or a surfactant or a combination of acid or alkali and surfactant and the treatment is continued until the waxy or silica layers are sufficiently removed so as not to interfere with the bond to the binder.

2. A process according to claim 1 in which the agent is a combination of strong acid or alkali and surfactant.

3. A process according to claims 1 and 2 in which the agent is applied in an aqueous medium.

4. A process according to claim 1 in which the agent is an alkali and the process is carried out in the absence of simultaneous treatment with a high shear attrition system, or the agent is an alkali with surfactant and the process is carried out in the presence of a simultaneous treatment with a high shear attrition system.

5. A process according to claim 1 in which the agent is an acid or non-alkaline surface active agent that is carried out in the presence or the absence of a high shear attrition system.

6. A process for the treatment of annual plant material to improve the bondability to synthetic or natural binders comprising subjecting the material to treatment with a surfactant agent in a liquid acidic or alkaline dispersion before or during at least part of an attrition

treatment of the fibres.

7. A process according to claim 5 wherein the attrition treatment is a high shear treatment.

8. A method according to any one of claims 1 to 7 in which the waxy and silica layers are removed to provide a water absorption of at least 200% weight gain.

INTERNATIONAL SEARCH REPORT

Inte   onal Application No
PCT/GR 98/00021

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B27N1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B27N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 709 569 A (LOUIS GRAND) 26 May 1954 cited in the application see page 1, right-hand column, line 52 - page 2, right-hand column, line 91; claims; example 2 ---	1-4
X	GB 2 084 212 A (23 SZ ALLAMI EPITOIPARI VALLAL) 7 April 1982 cited in the application see page 1, line 23 - line 30; claims ---	1,3,4
A	WO 93 25358 A (SUNDS DEFIBRATOR IND AB ;SAEFSTROEM CHRISTER (SE); MIKAELSSON ARON) 23 December 1993 cited in the application ---	
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Inte onal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 91 12367 A (SCA RESEARCH AB) 22 August 1991 cited in the application ---	
A	DE 42 11 888 A (BONIN WULF V DR) 14 October 1993 cited in the application -----	

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/GR 98/00021

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 709569 A		NONE	
GB 2084212 A	07-04-1982	AT 381925 B	10-12-1986
		AT 394181 A	15-05-1986
		CH 653078 A	13-12-1985
		DE 3136521 A	09-06-1982
		FR 2490142 A	19-03-1982
		IN 154800 A	15-12-1984
WO 9325358 A	23-12-1993	SE 470330 B	24-01-1994
		AT 143625 T	15-10-1996
		AU 662432 B	31-08-1995
		AU 4363393 A	04-01-1994
		CA 2136537 A	23-12-1993
		CN 1079687 A,B	22-12-1993
		CZ 9403088 A	14-06-1995
		DE 69305165 D	07-11-1996
		DE 69305165 T	06-03-1997
		DK 647174 T	13-01-1997
		EP 0647174 A	12-04-1995
		ES 2095060 T	01-02-1997
		FI 945790 A,B,	09-12-1994
		HR 930967 A	30-04-1995
		HU 69072 A,B	28-08-1995
		IL 105811 A	31-12-1995
		JP 7507735 T	31-08-1995
		NO 944779 A	09-12-1994
		NZ 253367 A	27-11-1995
		PL 170405 B	31-12-1996
		RU 2083359 C	10-07-1997
		SE 9201800 A	12-12-1993
		SI 9300293 A	31-03-1994
		SK 153094 A	10-05-1995
		ZA 9304108 A	13-01-1994
WO 9112367 A	22-08-1991	SE 466060 B	09-12-1991
		AT 122420 T	15-05-1995
		AU 647780 B	31-03-1994
		AU 7327191 A	03-09-1991
		CA 2073763 A	14-08-1991

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte ional Application No
PCT/GR 98/00021

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9112367 A		DE 69109696 D	14-06-1995
		DE 69109696 T	14-09-1995
		DK 572388 T	28-08-1995
		EP 0572388 A	08-12-1993
		ES 2072603 T	16-07-1995
		FI 923605 A,B,	12-08-1992
		JP 5503966 T	24-06-1993
		NO 302624 B	30-03-1998
		SE 9000515 A	14-08-1991
		US 5607546 A	04-03-1997
DE 4211888 A	14-10-1993	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)